<Division of Materials Chemistry> Chemistry of Polymeric Functionality Materials

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http://www.scl.kyoto-u.ac.jp/~kohjshin/index.htm

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Visitors

Dr KRACOVSKY, Ivan	Charles University, Czech Republic, 30 August 2004 - 26 August 2005
Dr MAGONOV, Sergei	Digital Instruments/Veeco, USA, 15 July 2005
Dr LIZ-MARZÁN, Luis M	University of Vigo, Spain, 26 July 2005

Scope of Research

Relationships between molecular arrangements in polymeric functionality materials and their properties are investigated. Formation mechanisms of higher order structures are elucidated by electron microscopy and X-ray diffraction measurements. The major research subjects are as follows: (1) Strained-induced crystallization of natural rubber, (2) Ionic conductivity of uniaxially stretched elastomer, (3) Direct observation of molecular chains in the epitaxially grown lamellar crystals of polymers, (4) Polymer gel consisting of the stereoregular polystyrene and (5) Spontaneous nano-scale patterning on uniaxially oriented polymer layers.

Research Activities (Year 2005)

Presentations

"Three-Dimensional Dispersion of Nano-Fillers in Soft Nano-Composite as Revealed by 3D-TEM / Electron Tomography", Kohjiya S, Materials 2005, 7th Portuguese Materials Society Meeting, 3rd International Materials Symposium, Aveiro, Portugal, 20 - 23 March.

"Smart Nano-Composite: Strain-Induced Crystallization of Natural Rubber", Kohjiya S, 10th International Seminar on Elastomers, Rio de Janeiro, Brasil, 5 - 8 April.

"Nano-Structural Elucidation in Carbon Black Loaded NR Vulcanizate by 3D-TEM and In Situ WAXD Measurements", Kohjiya S, Kato A, Shimanuki J, Ikeda Y, Tosaka M, Poompradub S, Toki S, Hsiao B S, Spring 167th Technical Meeting of the Rubber Division, ACS, San Antonio, Texas, USA, 16 - 18 May, and other 1 presentation.

"Morphological Study on Uniaxially Oriented Thin Films of Polyesters", Yoshioka T, Fujimura T, Tsuji M, Kohjiya S, Kawahara Y, 54th SPSJ Annual Meeting, Yokohama, Japan, 25 - 27 May, and other 11 presentations.

"Dynamical Study on Strain-Induced Crystallization of Natural Rubber Networks: Behavior as a Smart Nanocomposite", Kohjiya S, 5th International Symposium Molecular Mobility and Order in Polymer Systems, St. Petersburg, USA, 20 - 24 June.

"Physical Gelation of Syndiotactic Polystyrene in the Presence of Poly(Ethylene Oxide)", Senoo K, Matsuda S, Kohjiya S, The International Rubber Conference 2005 Yokohama, Yokohama, Japan, 24 - 28 October.

Grants

Kohjiya S, Stress-Induced Crystallization Behavior of Natural Rubber, Grant-in-Aid for Scientific Research, (B) (2), 1 April 2003 - 31 March 2005.

Tsuji M, High-resolution TEM of the Shish-Kebab Structure in Uniaxially Oriented Polyesters, Grant-in-Aid for Scientific Research, (C) (2), 1 April 2004 - 31 March 2007.

Morphological Study on Uniaxially Oriented Thin Films of PBT

The molecular weight of aromatic polyesters falls off easily in the molten state, mostly due to the transesterification reaction. Accordingly, the formation of the shish-kebab structure consisting of central extended-chain crystal and folded-chain crystals has been considered to be fairly difficult. We prepared uniaxially oriented thin films of poly(butylene terephthalate) (PBT), one of aromatic polyesters, by applying shear strain to the melt and studied their resulting morphology by transmission electron microscopy. Formation of stacked-lamellar structures in this aromatic polyester was visually evidenced. On the basis of crystallographic consideration, we assigned each of the recognized stacked-lamellar structures to a shish-kebab structure or a part of it. In addition, we successfully demonstrated that, in one shish-kebab structure, all or almost all kebabs (namely, lamellae) have a same crystallographic orientation. Fig. 1 is a set of dark-field images obtained from the same specimen region. In the left side (untilted) image, no remarkable morphology is recognized, while in the right side image tilted by 15°, some stacked-lamellar structures are observed. This change in appearance of the stacked lamellar structures, depending on the direction of the incident electron beam, suggests that all of the lamellae in one observed group as a stacked-lamellar structure have a same crystallographic orientation against the direction of incident electron beam.

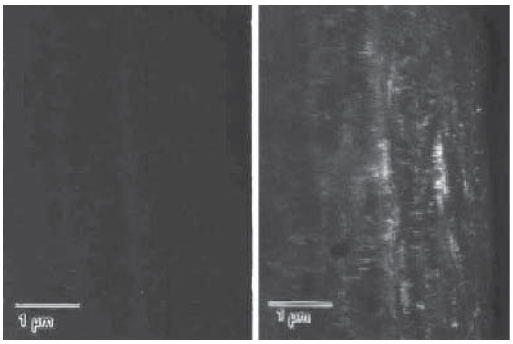

Figure 1. Dark-field images of PBT taken from the same specimen area: (left) un-tilted and (right) tilted by 15° around the vertical axis (shearing direction). Both images were taken mainly by using a 100 reflection of the α form. The shearing direction is vertical.

Self-Assembly of Nano-Sized Arrays on Highly Oriented Thin Films of Poly(Tetrafluoroethylene)

Self-assembly of nano-sized arrays by casting a dilute solution of a guest material on the friction-transferred poly(tetrafluoroethylene) (FT-PTFE) substrate was newly discovered. Long axis of the rod-like structures forming the arrays is aligned perpendicular to the chain direction of FT-PTFE, and accordingly, the arrays are highly anisotropic. This phenomenon was observed for aqueous or organic solutions of polymers or organic materials. The arrays in question are formed regardless to the crystallinity of the guest materials. The formation mechanism of the nano-sized arrays is still unclear. However, we guess that they are formed as a result of microscopic flow pattern at the edge of the solution film, according to the observation of the dynamic structure in the drying solution by optical microscopy. The arrays in question may be a new type of dissipative structure. If formation of the nano-sized arrays can be controlled, this phenomenon may be applicable to fabrication of, e.g., optical devices.

Figure 2. Nano-sized arrays prepared from atactic polystyrene. Scale bar is 500 nm. The molecular chains of PTFE are oriented vertically.

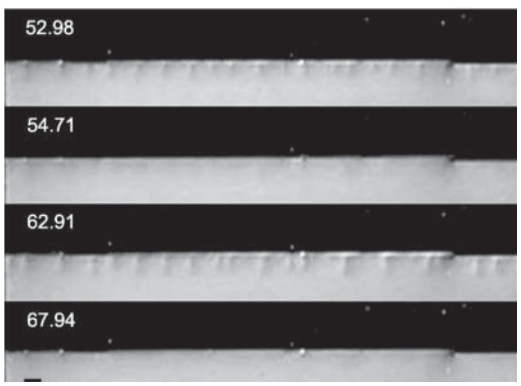

Figure 3. Time series of a drying film of a dilute solution of atactic polystyrene. Elapsed time (sec) is indicated at the left side of each part. The FT-PTFE / glass surface is exposed in the upper dark area, while the lower bright area is covered by the solution. The molecular chains of PTFE are oriented horizontally. Scale bar is 10 μm.